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     FILE 'CAPLUS' ENTERED AT 15:25:49 ON 13 MAY 2004
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L1          220 S E6-E7
                E TOKUNAGA MAKOTO/AU
L2           55 S E3
                E LARROW JAY/AU
L3           19 S E4-E5
L4          277 S L1 OR L2 OR L3
L5           39 S L4 AND KINETIC(W)(RESOLUTION OR RESOLN)
L6            0 S L5 AND SILYL(W)AZIDE
L7            0 S KINETIC(L)(RESOLUTION OR RESOLN) AND SILYL(W)AZIDE
L8           64 S KINETIC(L)(RESOLUTION OR RESOLN) AND AZIDE
L9            2 S L8 AND CHIRAL(W)CATALYST

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=> d 1-2 bib abs
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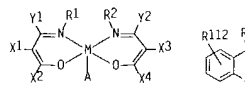
L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1999:722857 CAPLUS
DN 131:350871
TI Chiral non-racemic catalysts containing Main-group metals and tridentate or tetradentate ligands for asymmetric nucleophilic addition reactions to π bonds
IN Jacobsen, Eric N.; Sigman, Matthew S.
PA President and Fellows of Harvard College, USA
SO PCT Int. Appl., 90 pp.
CODEN: PIXXD2
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 9956699	A2	19991111	WO 1999-US9570	19990430
	WO 9956699	A3	20000518		
	W: CA, JP				
	RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
	US 6521561	B1	20030218	US 1998-71842	19980501
	CA 2329316	AA	19991111	CA 1999-2329316	19990430
	EP 1073613	A2	20010207	EP 1999-922765	19990430
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI				
	JP 2002513734	T2	20020514	JP 2000-546729	19990430
	US 2003187249	A1	20031002	US 2002-325592	20021220
PRAI	US 1998-71842	A	19980501		
	WO 1999-US9570	W	19990430		

OS CASREACT 131:350871; MARPAT 131:350871
GI

L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN (Continued)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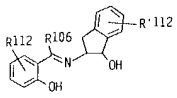
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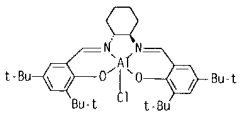
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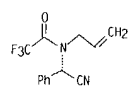

IV

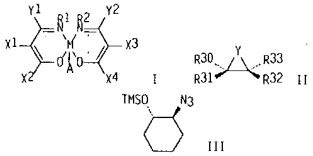
AB The present invention relates to a method and catalysts for the stereoselective addition of a nucleophile to a reactive π-bond of a substrate. Claimed is a stereoselective nucleophilic addition reaction of a π-bond-containing substrate with a nucleophile in the presence of a chiral, non-racemic catalyst to produce a stereoisomerically enriched addition product. The substrate comprises a C-C or C-heteroatom π-bond, and the nucleophile comprises at least one pair of Lewis basic electrons. The chiral, non-racemic catalysts of the invention constitute the first examples of catalysts for nucleophilic addns. that comprise a Main-group metal and a tri- or tetradentate ligand. One of a number of preferred chiral non-racemic catalysts of the invention includes metallosalenates I (R1, R2, Y1, Y2, X1-X4 = H, halo, alkyl, alkenyl, alkynyl, OH, alkoxy, siloxy, amino, nitro, SH, amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, etc., or any two or more taken together form a 4-8 membered carbocycle or heterocycle which may be a fused ring, with a proviso that requires the β-iminocarbonyls as tetradentate ligand). Other preferred chiral non-racemic catalysts of the invention include various metalloporphyrinates or porphyrin-like complexes, complexes of the tridentate chiral Schiff base ligand II (R106 = H, halo, alkyl, etc.; each R112, R'112 is absent or represents one or more covalent substitutions of the heterocycle to which it is attached), or complexes of various tetradentate azamacrocycles. Catalysts may contain a Main-group metal selected from Groups 1, 2, 12, 13, or 14 of the periodic table. The catalyst may be immobilized on an insol. matrix. The nucleophilic addition reaction may be enantioselective, diastereoselective, or a

L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN (Continued)
diastereoselective reaction which is a **kinetic resoln.** The π-bond-contg. substrate may include, e.g., aldehydes, conjugated enals, thioaldehydes, conjugated thioenals, selenoaldehydes, conjugated selenoenals, ketones, conjugated enones, thioketones, conjugated thioenones, selenoketones, conjugated selenoenones, imines, oximes, hydrazones, glyoxylates, pyruvates, conjugated enoates, α,β-unsatd. amides, α,β-unsatd. imides, lactones, thionolactones, thiolactones, dithiolactones, lactams, and thiolactams. The reacting nucleophiles may include conjugate bases of weak Bronsted acids, e.g., cyanide, **azide**, isocyanate, thiocyanate, alkoxide, thioalkoxide, carboxylate, thiocarboxylate, and carbanions. A highly enantioselective hydrocyanation reaction is achieved by this method. Treatment of N-allylbenzaldimine with HCN in the presence of chiral (salen)Al(III) complex III (toluene, -70°, 15 h) followed by workup with TFAA affords (S)-(+)-trifluoroacetamide IV in 91% yield, 95% ee. The asym. Strecker-type reaction catalyzed by III provides a straightforward entry into enantiomerically enriched α-amino acid derivs. Also claimed are **chiral catalysts** comprising a main-group metal atom or ion, and an asym. tetradentate or tridentate ligand wherein the catalyst catalyzes at least one asym. reaction. The asym. reactions may comprise epoxidn., aziridination, cycloaddn., sigmatropic rearrangement, addn. of nucleophiles to π bonds, ring-opening reactions, hetero-Diels-Alder or hetero-ene reactions, Claisen rearrangements, carbonyl redns., and addn. of nucleophiles to carbonyl groups or to C:N π bonds.

L9 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1999:468087 CAPLUS
DN 131:129576
TI Stereoselective epoxy ring opening reactions using chiral transition metal-salen complexes
IN Jacobsen, Eric N.; Leighton, James L.; Martinez, Luis E.
PA President and Fellows of Harvard College, USA
SO U.S., 45 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 4

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5929232	A	19990727	US 1996-622549	19960325
	US 5665890	A	19970909	US 1995-403374	19950314
	CA 2213007	AA	19960919	CA 1996-2213007	19960314
	US 6262278	B1	20010717	US 1998-134393	19980814
	US 2002032338	A1	20020314	US 2001-899516	20010705
	US 6448414	B2	20020910		
	US 2003139614	A1	20030724	US 2002-206143	20020726
	US 2004044233	A1	20040304	US 2003-615501	20030707
PRAI	US 1995-403374	A2	19950314		
	US 1996-622549	A2	19960325		
	US 1998-134393	A1	19980814		
	US 2001-899516	A1	20010705		
	US 2002-206143	A1	20020726		

OS CASREACT 131:129576; MARPAT 131:129576
GI


I II III

AB The present invention relates to a **kinetic resolution** process for stereoselective or regioselective chemical synthesis which generally comprises reacting a nucleophile and a chiral or prochiral cyclic substrate in the presence of a non-racemic **chiral catalyst** to produce a stereoisomerically or regioselectively enriched product. Said **chiral catalyst** comprises an asym. tetradentate ligand complexed with a metal atom, which complex has a

L9 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN (Continued)
rectangular planar or rectangular pyramidal geometry, e.g. metal-salen complexes (I; R1, R2, Y1, Y2, X1, X2, X3, X4 = hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, seleno ethers, ketones, aldehydes, esters, or (CH2)mR7, or any two or more of the substituents taken together form a carbocyle or heterocycle ring having from 4 to 8 atoms in the ring structure; wherein R7 = aryl, cycloalkyl, cycloalkenyl, heterocycle, polycycle; m = 0 or an integer in the range of 1 to 8; M = the late transition metal; A = a counterion or a nucleophile; provisos given). The substrates are epoxides, thioepoxides, aziridines, or cyclopropanes represented by general formula [II; Y = O, S, NR50, C(R52)(R54), A-B-C; wherein R50 = hydrogen, alkyl, carbonyl-substituted alkyl, carbonyl-substituted aryl, a sulfonate; R52, R54 = an electron-withdrawing group; A, C = absent, C1-5 alkyl, O, S, carbonyl, or NR50; B = carbonyl, thiocarbonyl, phosphoryl, sulfonyl; R30, R31, R32, R33 = org. or inorg. substituent which form a covalent bond with the C1 or C2 carbon atoms of 1-8, and which permit formation of a stable ring structure including Y]. Thus, cyclohexene oxide was added to a mixt. of chromium-salen complex, (R,R)-[1,2-bis(3,5-di-tert-butylsalicylideneamino)cyclohexane]-chromium (III) chloride (prepn. given) (2 mol%), and Et2O and stirred for 15 min, followed by adding Me3SiN3. The resulting brown soln. was stirred at room temp. for 28 h to give 80% 2-azidocyclohexanol (III) of 94% ee.
RE.CNT 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

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=> s l8 and catalyst
        655601 CATALYST
        659980 CATALYSTS
        839866 CATALYST
                (CATALYST OR CATALYSTS)
L10     ·    20 L8 AND CATALYST

=> s l10 not l9
L11         18 L10 NOT L9

=> d 1-18 bib abs
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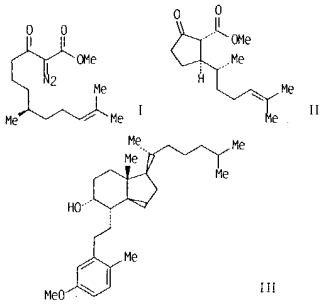
L11 ANSWER 1 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2004:270944 CAPLUS
TI Enzymatic dynamic **kinetic resolution** of epihalohydrins
AU Lutje Spelberg, Jeffrey H.; Tang, Lixia; Kellogg, Richard M.; Janssen, Dick B.
CS Groningen Biomolecular Sciences and Biotechnology Institute, Department of Biochemistry, University of Groningen, Groningen, 9747 AG, Neth.
SO Tetrahedron: Asymmetry (2004), 15(7), 1095-1102
CODEN: TASYE3; ISSN: 0957-4166
PB Elsevier Science B.V.
DT Journal
LA English
AB The haloalc. dehalogenase from Agrobacterium radiobacter AD1 catalyzes the reversible ring closure of vicinal haloalcs. to produce epoxides and halides. In the ring opening of epoxides, non-halide nucleophiles such as N3- are accepted. The enantioselective irreversible ring opening of an epihalohydrin by N3-, combined with racemization caused by a reversible ring opening by a halide, resulted in an enzymic dynamic **kinetic resolution** yielding optically active (S)-1-azido-3-halo-2-propanol. With epichlorohydrin as a substrate, the rate of ring opening by N3- was higher than the rate of racemization, resulting in a mixed **kinetic resolution** and dynamic **kinetic resolution**. With epibromohydrin as the substrate, the racemization rate was higher than the rate of ring opening, resulting in an efficient dynamic **kinetic resolution**. By optimizing the pH of the medium and the concns. of N3- and Br-, the product (S)-1-azido-3-bromo-2-propanol could be obtained in 84% yield and 94% ee. An (R)-enantiomer selective ring closure of this bromoalc., catalyzed by the same enzyme, caused a simultaneously occurring **kinetic resolution**, yielding when the conversion progressed, an increase in enantiopurity of (S)-1-azido-3-bromo-2-propanol to >99% ee with a yield of 77%. This compound and the ring-closed product glycidyl azide can be used as chiral synthetic building blocks.
RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 2 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2004:56131 CAPLUS
DN 140:259747
TI Secondary Deuterium **Kinetic** Isotope Effect for Aquation, Solvolysis, and Isomerization Reactions of trans-[Co(en)2(OSMe2)N3]2+, and the **Resolution** of a Mechanistic Anomaly
AU Jackson, W. G.
CS School of Physical Environmental and Mathematical Sciences, Chemistry University College (UNSW), Australian Defence Force Academy, Canberra, 2600, Australia
SO Inorganic Chemistry (2004), 43(8), 2577-2584
CODEN: INOCAJ; ISSN: 0020-1669
PB American Chemical Society
DT Journal
LA English
AB The two closely spaced NH signals in the 1H NMR spectrum of trans-[Co(en)2(OSMe2)(N3)]2+ have been reassigned using 2D NMR and other techniques. Thus, the unusual syn to anti (to Co-N3) NH rearrangement on base catalyzed substitution of the selectively deuterated complex in ND3(l) has been reinterpreted as "normal", with inversion of the effective deprotonation site accompanying the act of substitution. The re-examination of this system required a repeat study of the secondary isotope effect for the acid hydrolysis reaction, previously used to assign syn and anti amine sites, and this has been extended to other solvents (Me2SO, MeCN). The relative NH proton exchange rates are also reconsidered. A systematic rate reduction for Me2SO substitution is observed for deuterium incorporation into the cis-NH centers, irresp. of whether these are syn or anti, and the effect is much greater in Me2SO than in water. The results are interpreted in terms of zero point energy effects and coupled vibrations.
RE.CNT 26 THERE ARE 26 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 3 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2003:867324 CAPLUS
DN 140:93659
TI CrIII(salen) impregnated on silica for asymmetric ring opening reactions and its recovery via desorption/re-impregnation
AU Dioos, Bart M. L.; Jacobs, Pierre A.
CS Centre for Surface Chemistry and Catalysis, K.U. Leuven, Heverlee, 3001, Belg.
SO Tetrahedron Letters (2003), 44(49), 8815-8817
CODEN: TELEAY; ISSN: 0040-4039
PB Elsevier Science B.V.
DT Journal
LA English
AB The impregnation of CrIII(salen) complexes on silica resulted in a heterogeneous **catalyst** for the asym. ring opening (ARO) reaction of epoxides with good selectivity and acceptable activity. As became apparent from a series of 10 successive batch tests in the ARO reaction of 1,2-epoxyhexane, leaching was limited, while catalytic activity and selectivity were acceptable. Though the support suffered from abrasion in the batch reactor, 80% of the **catalyst** was easily recoverable via simple extraction from the used solid **catalyst** and entirely transferable onto a fresh carrier via impregnation. It was shown that 80% of the leached **catalyst** at the end of the tests could be transformed into a fresh heterogeneous **catalyst** as well.
RE.CNT 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 4 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2002:502361 CAPLUS
DN 137:384429
TI Exploration of the biocatalytic potential of a halohydrin dehalogenase using chromogenic substrates
AU Lutje Spelberg, Jeffrey H.; Tang, Lixia; van Gelder, Marc; Kellogg, Richard M.; Janssen, Dick B.
CS Groningen Biomolecular Sciences & Biotechnology Institute, Department of Biochemistry, University of Groningen, Groningen, 9747 AG, Neth.
SO Tetrahedron: Asymmetry (2002), 13(10), 1083-1089
CODEN: TASYE3; ISSN: 0957-4166
PB Elsevier Science Ltd.
DT Journal
LA English
AB Halohydrin dehalogenases are bacterial enzymes that catalyze the reversible formation of epoxides from vicinal halohydrins. A spectrophotometric assay for halohydrin dehalogenases based on the absorption difference between the halohydrin para-nitro-2-bromo-1-phenylethanol and the epoxide para-nitrostyrene oxide was developed. The enantioselectivity of ring-closure reactions catalyzed by three different halohydrin dehalogenases could be estimated from the shape of progress curves. Evaluation of ring-opening reactions catalyzed by halohydrin dehalogenase from Agrobacterium radiobacter AD1 established that, in addition to Cl- and Br-, nucleophiles such as N3-, CN- and NO2- are also accepted for the ring opening of para-nitrostyrene oxide. The ring-opening reactions with these nucleophiles resulted in highly enantioselective **kinetic resolns.**, which expands the scope of synthetically valuable conversions catalyzed by a halohydrin dehalogenase.
RE.CNT 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 5 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2001:27682 CAPLUS
DN 134:208005
TI Synthesis of (-)-Astrogorgiadiol
AU Taber, Douglass F.; Malcolm, Scott C.
CS Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, 19716, USA
SO Journal of Organic Chemistry (2001), 66(3), 944-953
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
OS CASREACT 134:208005
GI



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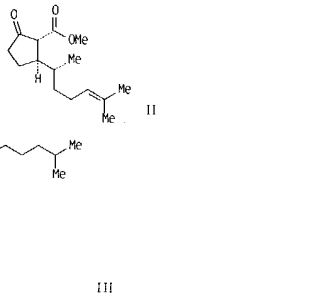


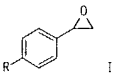
II

III

AB Reaction of Rh2(S)-PTPA4 with the (R)-citronellol-derived α-diazo-β-ketoester I led to the formation of cyclic β-ketoester II in 95% yield and 48% diastereomeric excess. The purity of II was increased to >99% de after one crystallization. To demonstrate its utility in steroid total synthesis, the β-ketoester II was carried on to secosteroid (-)-astrogorgiadiol (III), a naturally occurring vitamin D analog with antiproliferative properties.
RE.CNT 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD

L11 ANSWER 5 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN (Continued)
ALL CITATIONS AVAILABLE IN THE RE FORMAT

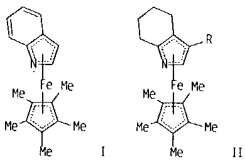
L11 ANSWER 6 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2000:866575 CAPLUS
DN 134:178304
TI Highly enantioselective and regioselective biocatalytic azidolysis of aromatic epoxides
AU Spelberg, Jeffrey H. Lutje; van Hylckama Vlieg, Johan E. T.; Tang, Lixia; Janssen, Dick B.; Kellogg, Richard M.
CS Department of Biochemistry Groningen Biomolecular Sciences and Biotechnology Institute and Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Groningen, 9747 AG, Neth.
SO Organic Letters (2001), 3(1), 41-43
CODEN: ORLEF7; ISSN: 1523-7060
PB American Chemical Society
DT Journal
LA English
OS CASREACT 134:178304
GI



I

AB The halohydrin dehalogenase from Agrobacterium radiobacter AD1 catalyzed the highly enantioselective and β-regioselective azidolysis of (substituted) styrene oxides I (R = NO2, Cl, H). By means of **kinetic resolns.** the remaining epoxide and the formed azido alc. could be obtained in very high ee. In a large scale conversion, the decrease in yield and selectivity due to the uncatalyzed chemical side reaction could be overcome by slow addition of **azide.**
RE.CNT 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 7 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2000:374233 CAPLUS
DN 133:135388
TI First synthesis and resolution of a planar-chiral tetrahydroindolyl complex of iron: Electronic tuning of reactivity and enantioselective nucleophilic catalysis
AU Suginome, Michinori; Fu, Gregory C.
CS Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA
SO Chirality (2000), 12(5/6), 318-324
CODEN: CHRLEP; ISSN: 0899-0042
PB Wiley-Liss, Inc.
DT Journal
LA English
OS CASREACT 133:135388
GI



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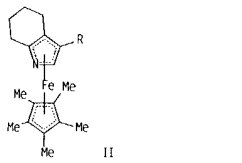


II

AB The 1st examples of an (η5-indolyl)iron complex (I) and (η5-tetrahydroindolyl)iron complexes (II; R = H (3), NMe2 (5)) are described. Reactivity studies establish that the (η5-tetrahydroindolyl)iron complexes are the most active azaferrocene-derived nucleophilic **catalysts** reported to date and that the reactivity of these complexes can be electronically tuned. Use of planar-chiral, enantiopure (η5-3-(dimethylamino)tetrahydroindolyl)FeCp* ((-)-5 or (+)-5) in asym. catalysis leads to stereoselectivities comparable to those furnished by a previously described azaferrocene complex.
RE.CNT 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 8 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2000:316228 CAPLUS
DN 133:30382
TI Asymmetric Catalysis of Epoxide Ring-Opening Reactions
AU Jacobsen, Eric N.
CS Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, 02138, USA
SO Accounts of Chemical Research (2000), 33(6), 421-431
CODEN: ACHRE4; ISSN: 0001-4842
PB American Chemical Society
DT Journal; General Review
LA English
AB A review with 37 refs. The discovery of the metal salen-catalyzed asym. ring-opening (ARO) of epoxides is chronicled. A screening approach was adopted for the identification of **catalysts** for the addition of TMSN3 to meso-epoxides, and the chiral (salen)CrN3 complex was identified as optimal. **Kinetic** and structural studies served to elucidate the mechanism of catalysis, which involves cooperative activation of both epoxide and **azide** by two different metal centers. Covalently linked bimetallic complexes were constructed on the basis of this insight, and shown to catalyze the ARO with identical enantioselectivity but 1-2 orders of magnitude greater reactivity than the monomeric analogs. Extraordinarily high selectivity is observed in the **kinetic resolution** of terminal epoxides using the (salen)CrN3/TMSN3 system. A search for a practical method for the **kinetic resoln**. reaction led to the discovery of highly enantiomer-selective hydrolytic ring-opening using the corresponding (salen)CoIII **catalyst**. This system displays extraordinary substrate generality, and allows practical access to enantiopure terminal epoxides on both laboratory and industrial scales.
RE.CNT 50 THERE ARE 50 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 9 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1999:753800 CAPLUS
DN 132:151334
TI The first chiral diimido chelate complexes of molybdenum and tungsten: transition metal diimido complexes on the way to asymmetric catalysis
AU Kretzschmar, Eike A.; Kipke, Jennifer; Sundermeyer, Jorg
CS Fachbereich Chemie, Philipps-Universitat Marburg, Marburg, D-35032, Germany
SO Chemical Communications (Cambridge) (1999), (23), 2381-2382
CODEN: CHCOFS; ISSN: 1359-7345
PB Royal Society of Chemistry
DT Journal
LA English
AB The first complexes [M(TADDAMINat)Cl2(dme)] [M = Mo (2), W (4)] containing a chiral diimido ligand regime have been synthesized; 2 has been structurally characterized and used as **catalyst** for C-C and C-N bond formation reactions.
RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

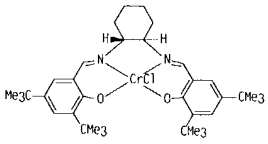
L11 ANSWER 10 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1999:655145 CAPLUS
DN 132:35320
TI Chromium catalyzed **kinetic resolution** of 2,2-disubstituted epoxides
AU Lebel, Helene; Jacobsen, Eric N.
CS Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, 02138, USA
SO Tetrahedron Letters (1999), 40(41), 7303-7306
CODEN: TELEAY; ISSN: 0040-4039
PB Elsevier Science Ltd.
DT Journal
LA English
OS CASREACT 132:35320
AB A chiral (salen)Cr(III) complex is an efficient **catalyst** for the **kinetic resolution** of 2,2-disubstituted epoxides. The **catalyst** thus used was azido[[2,2'-[(1R,2R)-1,2-cyclohexanediylbis[(nitrilo-κN)methylidyne]]bis[4,6-bis(1,1-dimethylethyl)phenolato-κO]](2-)]chromium. The scope and limitations of this methodol. are described.
RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 11 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1999:6421 CAPLUS
DN 130:196334
TI Epoxide hydrolases and their synthetic applications
AU Orru, Romano V. A.; Archelas, Alain; Furstoss, Roland; Faber, Kurt
CS Institute of Organic Chemistry, Graz University of Technology, Graz, A-8010, Austria
SO Advances in Biochemical Engineering/Biotechnology (1999), 63(Biotransformations), 145-167
CODEN: ABEBDZ; ISSN: 0724-6145
PB Springer-Verlag
DT Journal; General Review
LA English
AB Review with 103 refs. Chiral epoxides and 1,2-diols, which are central building blocks for the asym. synthesis of bioactive compds., can be obtained by using enzymes, i.e. epoxide hydrolases, which catalyze the enantioselective hydrolysis of epoxides. These biocatalysts have recently been found to be more widely distributed in fungi and bacteria than previously expected. Sufficient sources from bacteria, such as Rhodococcus and Nocardia spp., or fungi, such as Aspergillus and Beauveria spp., have now been identified. The reaction proceeds via an SN2-specific opening of the epoxide, leading to the formation of the corresponding trans-configured 1,2-diol. For the **resolution** of racemic monosubstituted and 2,2- or 2,3-disubstituted substrates, various fungi and bacteria have been shown to possess excellent enantioselectivities. Addnl., different methods, which lead to the formation of the optically pure product diol in a chemical yield far beyond the 50% mark (which is intrinsic to classic **kinetic resolns.**), are discussed. In addition, the use of non-natural nucleophiles such as **azides** or amines provides access to enantiomerically enriched vicinal azido- and amino-alcs. The synthetic potential of these enzymes for asym. synthesis is illustrated with recent examples, describing the preparation of some biol. active mols.
RE.CNT 102 THERE ARE 102 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 12 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1996:668537 CAPLUS
DN 126:8027
TI Dynamic **kinetic resolution** of epichlorohydrin via enantioselective catalytic ring opening with TMSN3. Practical synthesis of aryl oxazolidinone antibacterial agents
AU Schaus, Scott E.; Jacobsen, Eric N.
CS Dep. Chem. Chem. Biol., Harvard Univ., Cambridge, MA, 02138, USA
SO Tetrahedron Letters (1996), 37(44), 7937-7940
CODEN: TELEAY; ISSN: 0040-4039
PB Elsevier
DT Journal
LA English
OS CASREACT 126:8027
AB The dynamic **kinetic resolution** of racemic epichlorohydrin has been achieved via enantioselective asym. ring opening with TMSN3 catalyzed by the (salen) Cr(III)N3 complex 1. The resulting 3-azido-1-chloro-2-trimethylsiloxypropane product was obtained in high enantiomeric purity and incorporated into the synthesis of U-100592, a representative from a class of highly-promising aryl oxazolidinone antibacterial agents.

L11 ANSWER 13 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1996:435229 CAPLUS
DN 125:194962
TI **Kinetic Resolution** of Terminal Epoxides via Highly Regioselective and Enantioselective Ring Opening with TMSN3. An Efficient, Catalytic Route to 1,2-Amino Alcohols
AU Larrow, Jay F.; Schaus, Scott E.; Jacobsen, Eric N.
CS Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, 02138, USA
SO Journal of the American Chemical Society (1996), 118(31), 7420-7421
CODEN: JACSAT; ISSN: 0002-7863
PB American Chemical Society
DT Journal
LA English
OS CASREACT 125:194962
AB The (salen)Cr-catalyzed asym. epoxide ring opening reaction has been applied to the **kinetic resolution** of racemic terminal epoxides to provide 1-azido-2-trimethylsiloxyalkanes in 89-98% enantiomeric excess. The products are obtained in high yields and in excellent, often absolute, regiochem. purity. Epoxides bearing unbranched alkyl substituents were found to undergo **kinetic resoln**. with highest efficiency, with krel values well in excess of 100 for these substrates. The reaction also showed good functional group compatibility, with epoxides bearing chloride, alkoxide, and even Lewis basic cyano substituents displaying clean and highly enantioselective reactions. The utility of the ring-opened products as precursors to 1,2-amino alcs. was demonstrated by the synthesis of (S)-propranolol, a well-known antihypertensive agent, and of (R)-9-[2-(phosphonomethoxy)propyl]adenine, a compound recently shown to display prophylactic activity against SIV infection.

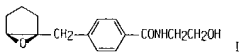
L11 ANSWER 14 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1995:569019 CAPLUS
DN 123:82537
TI Highly Enantioselective Ring Opening of Epoxides Catalyzed by (salen)Cr(III) Complexes
AU Martinez, Luis E.; Leighton, James L.; Carsten, Douglas H.; Jacobsen, Eric N.
CS Department of Chemistry, Harvard University, Cambridge, MA, 02138, USA
SO Journal of the American Chemical Society (1995), 117(21), 5897-8
CODEN: JACSAT; ISSN: 0002-7863
PB American Chemical Society
DT Journal
LA English
GI



I

AB The chiral (salen)Cr complex I is a highly effective **catalyst** for the enantioselective ring-opening of epoxides with Me3SiN3. In the presence of 2 mol % I, a variety of both functionalized and unfunctionalized meso epoxides were converted to their corresponding azido silyl ethers with ee's 81-98%. **Kinetic resolns.** of styrene oxide and epichlorohydrin were also accomplished with the same **catalyst** system. In addition, the ring-opening of meso epoxides proceeds cleanly in the absence of solvent and with undiminished enantioselectivity. Removal of product by distillation permitted the recovery of a **catalyst** that could be reused repeatedly in the asym. ring-opening reaction with enhanced reactivity yet identical enantioselectivity relative to I. This solvent-free reaction constitutes an example of an asym. catalytic process that generates product with high ee and the highest possible volumetric productivity, producing no waste whatsoever.

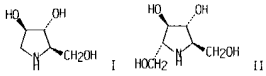
L11 ANSWER 15 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1993:495235 CAPLUS
DN 119:95235
TI Antibody-catalyzed enantioselective epoxide hydrolysis
AU Sinha, Subhash C.; Keinan, Ehud; Reymond, Jean Louis
CS Dep. Chem., Technion-Israel Inst. Technol., Haifa, 32000, Israel
SO Journal of the American Chemical Society (1993), 115(11), 4893-4
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA English
OS CASREACT 119:95235
GI



I

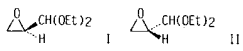
AB A monoclonal antibody catalyzed the acidic hydrolysis of epoxides to trans diols. This enzyme-like catalysis is evident from the Michaelis-Menten kinetics with multiple turnovers. The pH-rate profiles suggest that these are acid-catalyzed reactions, where epoxides normally open at the more substituted carbon. The competing reaction with nucleophiles, e.g., chloride, **azide**, aminoethanol, mercaptoethanol (all found to attack preferentially at the less substituted carbon atom), is not catalyzed by this antibody. A preparative scale hydrolysis of racemic epoxide I produces the trans diol with enantioselectivity of >98%. By contrast, both enantiomers of a smaller substrate are equally reactive with this catalytic antibody. These observations highlight the importance of secondary interactions between substrate and antibody and suggest that such interactions are a necessary feature to be built in to obtain efficient, enantioselective antibody **catalysts**.

L11 ANSWER 16 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1991:247627 CAPLUS
DN 114:247627
TI α-Amino aldehyde equivalents as substrates for rabbit muscle aldolase: synthesis of 1,4-dideoxy-D-arabinitol and 2(R),5(R)-bis(hydroxymethyl)-3(R),4(R)-dihydroxypyrrolidine
AU Hung, Rebecca R.; Straub, Julie Ann; Whitesides, George M.
CS Dep. Chem., Harvard Univ., Cambridge, MA, 02138, USA
SO Journal of Organic Chemistry (1991), 56(12), 3849-55
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
OS CASREACT 114:247627
GI



AB This work examined the application of rabbit muscle aldolase (RAMA) to stereospecific carbon-carbon bond formation in the preparation of carbohydrates containing amino groups. Several α-amino aldehyde equivs. were evaluated as substrates for RAMA and for their synthetic utility in transformations following the aldol reaction. This methodol. is illustrated by the syntheses of the pyrrolidine alkaloids 1,4-dideoxy-1,4-imino-D-arabinitol (I) and 2(R),5(R)-bis(hydroxymethyl)-3(R),4(R)-dihydroxypyrrolidine (II). The **kinetic resoln**. of racemic aldehydes by RAMA and mild methods for transforming the amino equivs. into the desired amines are discussed briefly.

L11 ANSWER 17 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1990:514960 CAPLUS
DN 113:114960
TI Enzymes in organic synthesis: synthesis of highly enantiomerically pure 1,2-epoxy aldehydes, epoxy alcohols, thiiranes, aziridine, and glyceraldehyde 3-phosphate
AU Pederson, Richard L.; Liu, Kevin K. C.; Rutan, James F.; Chen, Lihren; Wong, Chi Huey
CS Dep. Chem., Res. Inst. Scripps Clin., La Jolla, CA, 92037, USA
SO Journal of Organic Chemistry (1990), 55(16), 4897-901
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
OS CASREACT 113:114960
GI



AB An enzymic procedure for the synthesis of (R)- and (S)-glycidaldehyde di-Et acetal (I and II) is described. (±)-ClCH2CH(OAc)CH(OEt)2 was enantioselectively hydrolyzed by LP-80 lipase to give (S)-ClCH2CH(OH)CH(OEt)2 and (R)-ClCH2CH(OAc)CH(OEt)2, both in >95% calculated yield and >95% enantiomeric excess (ee). Both products were subsequently converted to epoxides I and II resp. Resolns. of (±)-ClCH2CH(OAc)CH2OCH2Ph and CH2CHCH2OCH2CH(OAc)CH2OSC6H4Me-p were similarly carried out to give the corresponding optically active 2-hydroxy and 2-acetoxy derivs. in 90% and >95% ee. These products were subsequently converted to the corresponding 1,2-epoxides. Nucleophilic opening of epoxide I was exemplified by the syntheses of (R)-N3CH2CH(OH)CH(OEt)2 and D-glyceraldehyde 3-phosphate. Conversion of the chiral epoxides to thiiranes and aziridines was also described.

L11 ANSWER 18 OF 18 CAPLUS COPYRIGHT 2004 ACS on STN
AN 1989:154053 CAPLUS
DN 110:154053
TI Metal(II) d-tartrates catalyzed asymmetric ring opening of oxiranes with various nucleophiles
AU Yamashita, Hiroyuki
CS Cent. Res. Inst., Mitsui Toatsu Chem., Inc., Yokohama, 247, Japan
SO Bulletin of the Chemical Society of Japan (1988), 61(4), 1213-20
CODEN: BCSJA8; ISSN: 0009-2673
DT Journal
LA English
OS CASREACT 110:154053
AB The asym. ring opening of meso-2,3-disubstituted oxiranes with thiols, PhNH2, and Me3SiN3 (I) was studied by the use of metal(II) d-tartrates as heterogeneous chiral Lewis acid **catalysts**. The enantioselectivity varied widely with the combination of oxirane, nucleophile, and metal(II) d-tartrate. Zn(II) d-tartrate gave the best enantioselectivity in the reactions of 1,2-epoxycyclohexane with 1-butanethiol, PhNH2, and I to afford the adducts in 85, 58, and 42% enantiomeric excess, resp. The **kinetic resolution** of racemic oxiranes with thiols catalyzed by Zn(II) d-tartrate was also studied.